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ANTIAROMATICITY IN RELATION TO
1,3,5,7-CYCLOOCTATETRAENE STRUCTURES

by

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An isodesmic energy analysis has been carried out at the MP2/6-31G**/HF/3-21G level for the non-planar ground state (1) of 1,3,5,7-cyclooctatetraene and for two planar forms, one having complete π delocalization (2) and the other having alternating single and double bonds (3). 1 is found to have a considerable degree of stabilization, which is attributed to limited π delocalization. The polyene 3 is the more stable of the two planar forms; it is a transition state in the inversion between two possible non-planar structures. 2 is found to be a triplet at the Hartree-Fock level, and is a critical point on an alternate pathway between the two possible arrangements of alternating single and double bonds in 3. Both 2 and 3 have negative isodesmic energies, indicating the presence of stabilizing factors.

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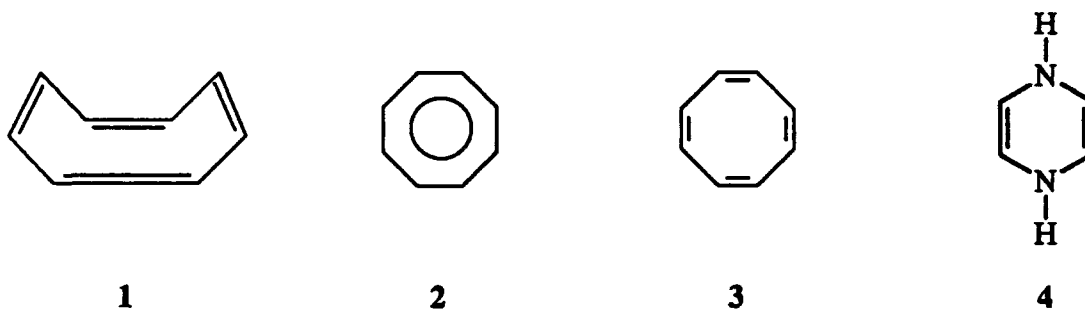
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Introduction

1,3,5,7-Cyclooctatetraene (1) is a non-planar, tub-shaped molecule with alternating single and double bonds. If it were planar, then extensive π -delocalization would be structurally feasible, with the conceivable limiting form being 2, in which all C-C bonds are equivalent. The latter would indeed be anticipated if the number of π electrons satisfied Hückel's $4n + 2$ rule ($n = 0, 1, 2, \dots$) [1,2]. However cyclooctatetraene has eight π electrons, which corresponds to a $4n$ situation; thus, in its planar conformation, it would fit into the antiaromatic category [2-5]. This term is applied to monocyclic fully-conjugated planar systems of $4n$ π electrons. Antiaromaticity is commonly viewed as being associated with a destabilizing effect; for cyclobutadiene, for instance, this has been reported as being at least 12 - 16 kcal/mole [6]. However in a recent computational study of 1,4-dihydropyrazine, 4, which is normally described as antiaromatic [7,8], we found evidence of significant *stabilization*, rather than the reverse [9].



Since it is sometimes implied that cyclooctatetraene is spared antiaromatic destabilization because of being nonplanar [2,5], we felt it would be interesting to investigate computationally any anomalous energetic effects in the systems 1 - 3; the last is the planar form with alternating single and double bonds. For this purpose we use the isodesmic reaction procedure, which is a well-established means for studying stabilizing and destabilizing factors in molecules [10,11]. An isodesmic reaction is a hypothetical chemical process in which the number of bonds of each formal type remains the same but their mutual relationships change. For instance, eq. (1) is an isodesmic reaction for 1:



The sign and magnitude of ΔE for an isodesmic reaction reflect any deviations from bond energy additivity; $\Delta E < 0$ indicates stabilizing factors in the molecule of interest and $\Delta E > 0$ implies destabilization. The value of ΔE depends of course upon the choice of reference molecules; a common practice is to take these to be the smallest ones containing the required bonds, as in eq. (1).

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Methods

The structures of 1 - 3 were optimized with GAUSSIAN 92 at the HF/3-21G level [12], followed by single point runs to obtain the corresponding MP2/6-31G* energies. The latter were used to compute the isodesmic energies. HF/3-21G normal mode vibrational frequencies were calculated for 2 and 3 in order to determine whether they correspond to local minima on the energy surface [11].

We have also used the electrostatic potential $V(r)$ as a probe of electronic delocalization. $V(r)$ is given rigorously by eq. (2),

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r') dr'}{|r' - r|} \quad (2)$$

in which Z_A is the charge on nucleus A, located at R_A , and $\rho(r)$ is the electronic density. $V(r)$ was computed at the HF/STO-5G//HF/3-21G level.

Results

Table 1 compares our HF/3-21G structure for 1 with the results for an experimental study [13]. The overall agreement is very good. In Table 2 are given the calculated relative and isodesmic energies, the C-C and C=C bond lengths, and the most negative electrostatic potentials (V_{\min}) for molecules 1 - 3. The data given for 2 are for the triplet state, which we found to be lower than the singlet by 8.2 kcal/mole, as expected from simple molecular orbital considerations.^{1,2,5} We confirmed that 3 is a singlet, at the HF/3-21G level; its triplet form was found to delocalize to 2.

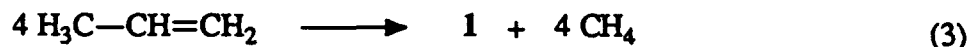
Cyclooctatetraene is found to be most stable in the non-planar form 1, in accord with experimental observation [13]. As has been pointed out [2], this allows the C-C-C angles to be closer to the 120° preferred by sp^2 -hybridized carbon than is possible with either 2 or 3, in which the ring angles are 135°. The bond lengths in 1 are close to what is typical for conjugated C-C and C=C bonds, about 1.46 Å and 1.32 Å respectively [14]. The electrostatic potential minima (V_{\min}) associated with the C=C double bonds are very similar to what we have found for ethylene, -13.1 kcal/mole [15].

3 is the more stable of the planar forms, but the vibrational frequency analysis shows it to have one imaginary value and to be a transition state in the inversion between the two possible tub-like conformations. 2 has two imaginary frequencies, and can be viewed as a critical point on an alternate pathway between the two possible arrangements of alternating single and double bonds in 3.

Discussion

Using eq. (1), the isodesmic energy obtained for **1** is -42.9 kcal/mole, indicating a considerable degree of stabilization which we attribute primarily to limited π delocalization. This also explains the fact that the C—C single bonds in **1** are shorter than is normal for their non-conjugated counterparts, which is about 1.53 Å [14].

Further insight into the bonding in **1** can be obtained by means of a different isodesmic reaction, eq. (3), in which the reference molecule is propene, $\text{H}_3\text{C}-\text{CH}=\text{CH}_2$. The latter is anticipated to already have some degree of π delocalization; indeed $\Delta E_{\text{isodesmic}}$ for propene relative to ethylene and ethane is -5.3 kcal/mole.



For **1**, $\Delta E_{\text{isodesmic}}$ for eq. (3) is -21.7 kcal/mole at the MP2/6-31G**/HF/3-21G level. Thus the stabilization of **1** is significantly more than a direct analogy to propene would suggest, presumably because each single C—C bond in **1** can gain delocalized π charge from two C=C double bonds rather than just one (as in propene). Consistent with this interpretation is the fact that the C—C distance in propene is 0.03 Å shorter than a typical unconjugated C—C single bond but yet 0.04 Å longer than in **1**.

The more stable planar form, **3**, clearly retains the polyene character of **1**; the bond lengths are remarkably similar, and the V_{min} values are intermediate between those of **1**. On the other hand, the ring bond lengths in **2** are very close to typical aromatic values (about 1.38 Å [14]) and the potential minima are located above and below the ring rather than near the bonds. For comparison, benzene has six minima of -10.6 kcal/mole above and below the ring [16].

It is interesting that eq. (1) gives both planar systems, **2** and **3**, negative isodesmic energies. This indicates the presence of stabilizing factors even in these molecules which have considerable bond angle strain, and certainly is not consistent with overall destabilizing effects. To put these magnitudes in perspective, the same approach applied to benzene leads to $\Delta E_{\text{isodesmic}} = -72.3$ kcal/mole. (If eq. (3) is applied to **2** and **3**, the resulting isodesmic energies are -2.6 and -6.6 kcal/mole, respectively.) Thus, our results for **3** show again [9] that an antiaromatic system need not necessarily show a net destabilization.

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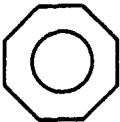
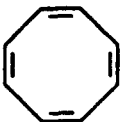
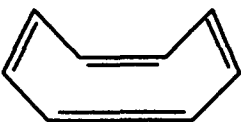
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Table 1. Comparison of calculated and experimentally-determined structures for 1,3,5,7-cyclooctatetraene. Distances are in Angstroms, angles in degrees.

Distance AB or angle ABC	HF/3-21G	Experimental ^a
C-C	1.477	1.462
C=C	1.320	1.334
C-H	1.077	1.090
C=C-C	126.4	126.46
C=C-H	118.5	118.3

^aReference 13.

Table 2. Calculated properties.

	Molecule	Relative energy, MP2/6-31G*// HF/3-21G, kcal/mole	$\Delta E_{\text{isodesmic}}$ MP2/6-31G*// HF/3-21G, kcal/mole [eq. (1)]	Bond length, Å	V_{min} HF/STO-5G// HF/3-21G, kcal/mole
2		19.1	-23.8	C-C: 1.390	-10.7 ^a
3		15.1	-27.8	C-C: 1.477 C=C: 1.323	-12.3 ^b
1		0	-42.9	C-C: 1.477 C=C: 1.320	-10.5 ^c -14.9 ^d

^aAt eight points above and below ring, on bisectors of bonds.^bAbove and below C=C double bonds.^cBelow C=C double bonds, outside of tub.^dAbove C=C double bonds, within tub.